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(54) Zeolites.

(57) A synthetic zeolite material, designated zeolite Nu-10,
having a molar composition expressed by the following formula:

0.5 to 1.5 R₂O : Y₂O₃ : at least 20 XO₂ : O to 4000 H₂O where-
in R is a monovalent cation or 1/n of a cation of valency n, X is
silicon and/or germanium, Y is one or more of aluminium, iron,
chrome, vanadium, molybdenum, arsenic, antimony, manga-
nese, gallium or boron, and H₂O is water of hydration additional
to water notionally present when R is H, and having a defined
X-ray pattern.

Zeolite Nu-10 is a useful catalyst for toluene methylation
and the like.

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Zeolites

The present invention relates to a novel zeolite material hereinafter referred to as zeolite Nu-10, to a method of making it and to processes using it as a catalyst.

According to the present invention, we provide a synthetic zeolite material, designated zeolite Nu-10, having a molar composition expressed by the following formula:
0.5 to 1.5 R_2O : Y_2O_3 : at least 20 XO_2 : 0 to 4000 H_2O
wherein R is a monovalent cation or $1/n$ of a cation of valency n, X is silicon and/or germanium, Y is one or more of aluminium, iron, chromium, vanadium, molybdenum, arsenic, antimony, manganese, gallium or boron, and H_2O is water of hydration additional to water notionally present when R is H, and having an X-ray pattern substantially as set out in Table 1 (as determined by standard technique using copper K α radiation).

Zeolite Nu-10 is characterised in part by its interplanar spacings as shown in Table 1. However, to characterise a zeolite fully, X-ray data alone is inadequate, and sorption and catalytic properties must also be taken into account. A further feature of

TABLE 1

X-Ray Data of Zeolite Nu-10

| d(A) | I |
|--------------|-----|
| 10.95 ± 0.25 | m→s |
| 8.80 ± 0.14 | w→m |
| 6.99 ± 0.14 | w→m |
| 5.41 ± 0.10 | w |
| 4.57 ± 0.09 | w |
| 4.38 ± 0.08 | vs |
| 3.69 ± 0.07 | vs |
| 3.63 ± 0.07 | vs |
| 3.48 ± 0.06 | m→s |
| 3.36 ± 0.06 | w |
| 3.31 ± 0.05 | w |
| 2.78 ± 0.05 | w |
| 2.53 ± 0.04 | m |
| 2.44 ± 0.04 | w |
| 2.37 ± 0.03 | w |
| 1.88 ± 0.02 | w |

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vs = 60 to 100
s = 40 to 60
m = 20 to 40
w = 0 to 20

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$$0.5 \text{ to } 1.5\text{R}_2\text{O} : \text{Y}_2\text{O}_3 : \text{at least } 60\text{XO}_2 : 0 \text{ to } 200 \text{H}_2\text{O}$$

The $\text{XO}_2/\text{Y}_2\text{O}_3$ ratio in Nu-10 is typically in the range

20 to 5000. The sodium/organo forms of Nu-10 appear to be most readily formed when this ratio is in the range

80 to 120. On the other hand, with potassium or rubidium

30 as inorganic cation, Nu-10 is most readily formed with a

$\text{XO}_2/\text{Y}_2\text{O}_3$ ratio in the range 40 to 1000.

2. STANDARDIZATION OF THE DATA



This definition includes both freshly prepared Nu-10 ("freshly prepared" means the product of synthesis, and washing, with optional drying, as hereinafter described) and also forms of it resulting from dehydration, and/or calcination, and/or ion exchange. In freshly prepared Nu-10, R may include an alkali metal cation, especially sodium, potassium, rubidium or caesium. Ammonium and hydrogen may also be present. Usually, or when prepared from nitrogen compounds, Nu-10 includes nitrogen-containing organic cations or bases as described below or cationic degradation products thereof, or precursors thereof. These nitrogen containing cations or bases are hereinafter referred to as Q.

The freshly prepared Nu-10 may also contain nitrogen-containing compounds well in excess of the 1.5 moles set out in the aforesaid definition of the composition of Nu-10 typically in the range 0.1 to 120 moles per mole of Y_2O_3 . Since Nu-10 is a zeolite, the nitrogen containing base must be physically trapped within the crystal lattice. It can be removed by thermal treatment and/or oxidative degradation or by displacement by suitable small molecules. This physically trapped basic material does not constitute part of the composition for the purposes of the definition. Thus Nu-10 as made typically has the following molar composition:

0.5 to 1.5 M_2O :0.1 to 120 Q: Y_2O_3 :20 to 5000 XO_2 :0 to 2000 H_2O

wherein M is an alkali metal and/or ammonium and can include hydrogen.

Among the ion-exchanged forms of zeolite Nu-10 the ammonium (NH_4^+) is of importance since it can be readily converted to the hydrogen form by calcination. The hydrogen form can also be prepared directly by exchange with an acid. The hydrogen-form and forms containing metals introduced by ion exchange are described further below.

15 These results and the results given in Table 2
suggest that zeolite Nu-10 has 10 ring ports which are a
tight fit for pyridine and p-xylene at 25°C. Both diffuse
in slowly after an initial modest uptake, suggesting a
substantial diffusion barrier exists at 25°C for these
20 molecules i.e. at about 5.85Å. The sorption of m-xylene
corresponds only to surface coverage on the zeolite Nu-10
powder. The slow uptake of n-hexane shows the channels
in Nu-10 present length barriers to molecules as well as
imposing restraints due to cross sectional areas. Thus
25 Nu-10 can be expected to show unique sorptive and catalytic
properties not hitherto seen in highly siliceous zeolites.
Zeolite Nu-10 should prove useful in separating aromatic
compounds especially isomers e.g. xylenes and ethylbenzene,
and in separating molecules not only on cross sectional
30 area differences, but also on length differences. It is
likely that substantial changes in separation processes and
in shape-selective catalytic processes can be achieved by
simply changing the temperature of operation and thus
modifying the effects of energy barriers to diffusion.

With the exception of the above, the following information is being furnished to you for your information only and is not to be used for any other purpose.

TABLE 2 - SORPTION ON HYDROGEN NU-10 (FROM EXAMPLE 12) AT 25°C

| Sorbate | Water | n-hexane | pyridine | p-xylene | m-xylene |
|-------------------------------|-------|----------|----------|----------|----------|
| Relative pressure P/po | 0.3 | 0.33 | 0.3 | 0.5 | 0.5 |
| Kinetic diameter σ_A^* | 2.7 | 4.3 | 5.8 | 5.85 | 6.0 |
| Sorption % w/w | | | | | |
| 10 min | 3.8 | 1.8 | 2.4 | 1.7 | 0.5 |
| 1 hour | 4.0 | 2.2 | 2.6 | 1.9 | |
| 2 hour | 4.0 | 2.4 | 2.7 | 2.0 | |
| 24 hour | | 4.5 | 5.8 | 3.0 | |
| 68 hour | 4.3 | 4.8 | 6.9 | 6.3 | 0.8 |

* Lennard Jones kinetic diameter (D W Breck, "Zeolite Molecular Sieves" Wiley Interscience (1974), p 636).

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TABLE 3 - VOIDAGE AVAILABLE IN HNU-10 AT 25°C

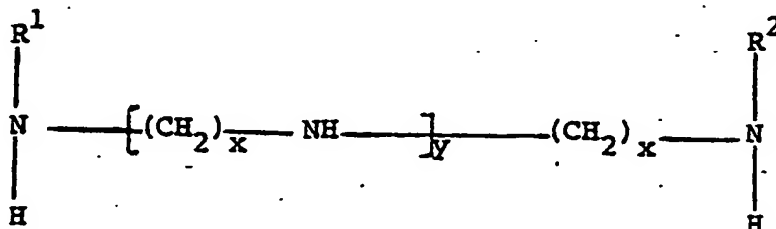
| Sorbate | Kinetic diameter σ_A | wt sorbed g/100g | Apparent voidage filled at equilibrium cc/100g |
|----------|--------------------------------|---------------------|---|
| water | 2.7 | 4.3 | 4.3 |
| n-hexane | 4.3 | 4.8 | 7.2 |
| pyridine | 5.8 | 6.9 | 7.1 |
| p-xylene | 5.85 | 6.3 | 7.2 |
| m-xylene | 6.0 | 0.8 | 0.9 |

Table 3 gives comparative data on apparent voidage filled by different sorbates assuming that all sorbates are adsorbed as liquids, with typical liquid densities at 25°C.

Zeolite Nu-10 is further characterised by its infra-red spectrum (shown in the attached drawing). In common with other zeolites, zeolite Nu-10 has two main IR absorption regions, viz. the stretch ν of the Si-O situated near to 1100 cm^{-1} and the deformation δ of the Si-O situated near to 500 cm^{-1} . Referring to the absorptions near to 1100 cm^{-1} , zeolite Nu-10 has three distinct absorptions at 1209 cm^{-1} medium, 1117 cm^{-1} strong and 1081 cm^{-1} strong. By comparison, the absorptions near to 1100 cm^{-1} for ZSM-5 are 1228 cm^{-1} (medium) and 1095 cm^{-1} (strong). Thus there is a significant difference both in position and number of absorptions of zeolite Nu-10 as compared with the absorptions of ZSM-5.

The deformations δ near to 500 cm^{-1} of Nu-10 again shows three characteristic, clearly defined absorptions at 637 cm^{-1} (weak), 547 cm^{-1} (weak) and 463 cm^{-1} (medium strong). By comparison, ZSM-5 has a doublet absorption at 545 cm^{-1} (medium) and 455 cm^{-1} (medium). The number of absorptions, their positions and relative intensities found in the infrared spectrum of zeolite Nu-10 are sufficient to identify Nu-10 and to distinguish it from ZSM-5.

Zeolite Nu-10 may be prepared by reacting an aqueous mixture containing at least one oxide XO_2 , at least one oxide Y_2O_3 and at least one polyalkylene polyamine having the formula:



where x is an integer from 2 to 6 and y is an integer from 0 to 10, provided that when y is 0, x is 2 to 5, an amine degradation product thereof, or a precursor thereof. In the polyamine, each of R^1 and R^2 , independently, represents hydrogen or a C_1 - C_6 alkyl group.

The reaction mixture preferably has the following molar ratios:

- XO_2/Y_2O_3 = 25 to 5000, preferably 40 to 1000, most preferred 80 to 500
- 10 M^1OH/XO_2 = 10^{-8} to 1.0, preferably 10^{-6} to 0.25, most preferred 10^{-4} to 0.15
- H_2O/XO_2 = 10 to 200, preferably 15 to 60, most preferred 30 to 50
- 15 Q/XO_2 = 0.05 to 4, preferably 0.1 to 1.0, most preferred 0.2 to 0.5
- M^2Z/XO_2 = 0 to 4.0, preferably 0 to 1.0, most preferred 0 to 0.6.

Zeolite Nu-10 can be prepared in the temperature range 50 to 250°C. The preferred range is 90 to 180°C and crystallization is carried out until substantially pure crystalline Nu-10 is obtained. Agitated reactions are preferred.

X is silicon or germanium, Y is aluminium, iron, chromium, vanadium, molybdenum, arsenic, antimony, manganese, gallium or boron, M^1 is an alkali metal or ammonium or hydrogen, M^2 is an alkali metal or ammonium or hydrogen and can be the same as M^1 and Q is the aforesaid polyalkylene polyamine, amine degradation product thereof or a precursor thereof, or a related compound. Z^- is a strong acid radical present as a salt of M^2 and may be added as a free acid to reduce the free M^1OH level to a desired value.

35 M^2Z addition, while not essential, can accelerate crystallization of zeolite Nu-10, and can also affect

the size of crystals obtained. It should be noted that addition of M^2Z can promote the formation of α -quartz and α -cristobalite, this can usually be avoided by reducing reaction times and/or temperature to minimise the chances of overrun. If M^2Z remains intercalated within the zeolite Nu-10 framework, then it can have substantial effects on the sorption and catalytic properties. M^1 and/or Q can be present as hydroxides or salts of inorganic or organic acids provided the M^1OH/XO_2 requirement is fulfilled.

The preferred polyalkylene polyamines are triethylene tetramine and tetraethylene pentamine.

The preferred alkali metal M^1 is sodium and/or potassium M^2 is preferably the same as M^1 or is hydrogen. The preferred oxide XO_2 is silica (SiO_2) and the preferred oxide Y_2O_3 is alumina (Al_2O_3).

The silica source can be any of those commonly considered for use in synthesising zeolites, for example powdered solid silica, silicic acid, colloidal silica or dissolved silica. Among the powdered silicas usable are precipitated silicas, especially those made by precipitation from an alkali metal silicate solution, such as the type known as "KS 300" made by AKZO, and similar products aerosil silicas, fume silicas and silica gels suitably in grades for use in reinforcing pigments for rubber or silicone rubber. Colloidal silicas of various particle sizes may be used, for example 10-15 or 40-50 microns, as sold under the Registered Trade Marks "LUDOX" "NALCOAG" and "SYTON". The usable dissolved silicas include commercially available waterglass silicates containing 0.5 to 0.6, especially 2.0 to 4.0 mols of SiO_2 per mol of alkali metal oxide, "active" alkali metal silicates as defined in UK Patent 1193254, and silicates made by dissolving silica in alkali metal hydroxide or quaternary ammonium hydroxide or a mixture thereof.

The alumina source is most conveniently sodium aluminate, but can be or can include aluminium, an aluminium salt for example the chloride, nitrate or sulphate, an aluminium alkoxide or alumina itself, which
5 should preferably be in a hydrated or hydratable form such as colloidal alumina, pseudoboehmite, boehmite, gamma alumina or the alpha or beta trihydrate.

The reaction mixture is reacted usually under autogenous pressure, optionally with added gas, e.g.
10 nitrogen at a temperature between 50 and 250°C until crystals of Nu-10 form, which can be from 1 hour to many months depending on the reactant composition and the operating temperature. Agitation is optional, but is preferable since it reduces the reaction time. If
15 agitation is inadequate, or the reaction is carried out under quiescent conditions, then there is a distinct probability of producing zeolite Nu-10 contaminated by ZSM5 family zeolites, such as zeolite Nu-4 of our copending UK Patent Application No. 8115407.

20 In order to prepare the best possible adsorbents and catalysts from zeolite Nu-10, it is essential that the levels of ZSM5 family zeolites are negligible, because ZSM5 family zeolites give rise to undesirable side effects as a result of their inferior shape-size-selectivity-performance as compared with the unique and
25 highly desirable properties of zeolite Nu-10 for certain applications, for example including but not limited to the separation of aromatic isomers, toluene methylation, and dehydration of alcohols.

30 The synthesis of zeolite Nu-10 in substantially pure form can be guaranteed by strict adherence to the narrow range conditions. For reaction mixture compositions in the wider ranges, substantially pure Nu-10 can still be obtained, especially where the more important narrow
35 range criteria such as XO_2/Y_2O_3 , M^1OH/XO_2 and temperature/time are met. Time/temperature becomes more critical in

the wider range and overrun to α -quartz and α -cristobalite becomes more likely. This tendency can be reduced by using potassium or rubidium as the alkali cations. To those skilled in the art it will be apparent, from examples given, that even in the wider reaction mixture ranges, many combinations will still give Nu-10 as the major component, and that with care it will be possible to prepare pure Nu-10.

If mixtures of zeolite Nu-10 and ZSM5 family zeolites are desired then this can be achieved by deliberately operating at XO_2/Y_2O_3 ratios below 70 and $NaOH/XO_2$ greater than 0.06.

At the end of the reaction, the solid phase is collected on a filter and washed and is then ready for further steps such as drying, dehydration and ion-exchange.

If the product of the reaction contains alkali metal ions, these have to be at least partly removed in order to prepare more acid forms of Nu-10 and this can be done by ion exchange with an acid, especially a strong mineral acid such as hydrochloric acid or by way of the ammonium compound, made by ion exchange with a solution of an ammonium salt such as ammonium chloride. Such ion exchange can be carried out by slurring once or several times with the solution.

In general, the cation(s) of zeolite Nu-10 can be replaced by any cation(s) of metals, and particularly those in Groups IA, IB, IIA, IIB, III (including rare earths) VIII (including noble metals) and by lead, tin and bismuth. (The Periodic Table is as in "Abridgements of Specifications" published by the UK Patent Office). Exchange is carried out using any water soluble salts containing the appropriate cation.

In order to prepare a catalyst, zeolite Nu-10 may be used in association with an inorganic matrix, or

with other materials which can be either inert or catalytically active. The matrix may be present simply as a binding agent to hold the small zeolite particles (0.005 to 10 microns) together, or it may be added as a diluent to control the amount of conversion in a process which may otherwise proceed at too high a rate, leading to catalyst fouling as a result of excessive coke formation. Typical inorganic diluents include catalyst support materials such as alumina, silica, kaolinic clays, bentonites, montmorillonites, sepiolite, attapulgite, Fullers earth, synthetic porous materials such as $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{SiO}_2\text{-ZrO}_2$, $\text{SiO}_2\text{-ThO}_2$, $\text{SiO}_2\text{-BeO}$, $\text{SiO}_2\text{-TiO}_2$ or any combination of these oxides. An effective way of mixing zeolite Nu-10 with such diluents is to mix appropriate aqueous slurries in a mixing nozzle and then to spray dry the slurry. Other ways of mixing can be used.

If zeolite Nu-10 in any cationic form or as a catalytic composite is exchanged or impregnated with hydrogenation/dehydrogenation components, such as Ni, Co, Pt, Pd, Re, Rh, hydrocracking and reforming catalysts can be made, especially if the Na_2O content is less than 0.1% w/w.

A wide range of hydrocarbon conversion catalysts can be prepared from zeolite Nu-10 by ion exchange or impregnation with cations, or oxides, selected from the following, Cu, Ag, Mg, Ca, Sr, Zn, Cd, B, Al, Sn, Pb, V, P, Sb, Cr, Mo, W, Mn, Re, Fe, Co, Ni and noble metals.

Usually, the Nu-10 catalyst will be in acid form thus stoichiometry is maintained by H^+ or H_3O^+ as an additional balancing cation, or as sole cation. Such catalysts may find application in the following processes: catalytic cracking, hydrodesulphurization, hydrodenitri-fication, catalytic dewaxing, alkylation of alkanes or aromatics, dealkylation, disproportionation, isomerisation of alkanes and alkyl benzenes, dehydration reactions, oxidation and polymerisation.

Particular mention may be made of an alkylation process which comprises contacting an alkyl-benzene or a mixture of alkylbenzenes and an alkylating agent under alkylating conditions in the vapour or liquid phase with a catalyst comprising zeolite Nu-10.

The alkylbenzene starting materials include toluene, ortho-, meta- and para-xylenes, ethylbenzene, trimethylbenzene, tetramethylbenzene, and the like, or mixtures thereof. The alkylating process is especially applicable to the use of toluene as the starting material.

Suitable alkylating agents include alkanols, alkyl halides, alkyl ethers, alkyl sulphides and olefins. Preferred methylating agents include methanol, methyl chloride, methyl bromide, methyl carbonate, dimethyl ether and dimethyl sulphide. The use of methanol as the methylating agent is especially preferred.

The molar ratio of the alkylating agent to the alkylbenzene is generally between about 0.005 and about 5, for example between about 0.1 and about 3.

An especially preferred alkylating process comprises the methylation of toluene using methanol as the methylating agent to give a product comprising the xylene isomers, and in particular to a process for the selective production of para-xylene from toluene and methanol, the said para-xylene being obtained in excess of its normal equilibrium concentration (which is about 23-24%) of the xylene isomers with limited production of higher methylbenzenes.

The alkylation process, e.g. methylation, is suitably carried out at a temperature in the range of about 250 to about 750°C, preferably about 350°C, to about 600°C, at a pressure between 1 atmosphere abs and about 60 atmosphere abs and at a WHSV of 1 to about 1500.

Mention may also be made of a process for the

production of hydrocarbons which comprises contacting a lower monohydric alcohol or an ether derived therefrom under conversion conditions with a catalyst comprising zeolite Nu-10.

5 Lower monohydric alcohols which may be used in this process particularly include saturated monohydric alcohols containing up to four carbon atoms in the molecule. Ethers which may be used include the symmetrical and unsymmetrical ethers derived from the aforesaid
10 alcohols by dehydration. If desired, mixtures of alcohols and/or ethers may be used. It is particularly preferred to use methanol and/or dimethyl ether as the starting material(s).

This process is suitably carried out at a temperature
15 in the range 250-700°C and preferably in the range 350-500°C. The pressure is suitably in the range 0.2-50 atm abs, preferably 0.5 to 20 atm abs. The weight hourly space velocity (WHSV) is typically in the range of about 0.5 to 50.

20 The products of the reaction, which include lower olefins, especially C₂ to C₇ olefins, particularly propylene and butylenes, and smaller amounts of some aromatic hydrocarbons such as benzene, toluene and xylenes, may be recovered and separated using conventional
25 methods.

The catalyst may be in the form of a fixed bed, fixed fluid bed or it may be of the transport type.

The catalyst as used maintains its activity for a substantial period, but can be regenerated by heating.
30 For example, when the catalyst is used in the form of a fluidised bed, the catalyst may be continuously withdrawn, passed through a regeneration zone and returned to the reaction.

35 Zeolite Nu-10 may also find applications in pollution control by its ability to remove organic con-

taminants from aqueous effluents.

The invention is illustrated by the following Examples.

Example 1

- 5 Preparation of sodium tetraethylene pentamine (TEPA)
Nu-10 and sodium Nu-10.

The synthesis mixture had the following molar composition:

- 2.34 Na_2O , 27 TEPA, Al_2O_3 , 96.6 SiO_2 , 3878 H_2O , 54.8 NaCl
10 38g TEPA were dispersed in 142g colloidal silica
(Syton X-30). Next, 1.6g sodium aluminate ($1.25 \text{Na}_2\text{O}$,
 Al_2O_3 , $3\text{H}_2\text{O}$) dissolved in 10g water were stirred into the
silica suspension followed by 23g sodium chloride
dissolved in 388g water. The resulting gel was mixed
15 thoroughly for $\frac{1}{2}$ hour to a homogeneous texture, and was
then reacted for 3 days at 180°C in a 1 litre stainless
steel stirred autoclave under autogenous pressure. The
stirrer speed was maintained at 500 rpm. After cooling
to about 60°C , the slurry was filtered and washed with
20 2 litres of distilled water at 60°C and dried overnight
at 120°C . The product was sodium TEPA Nu-10 with X-ray
diffraction data as shown in Table 4.

Example 2

- The product of Example 1 was calcined in moist air for
25 48 hours at 450°C and its X-ray diffraction pattern was
substantially unchanged. Next, it was slurry-exchanged
for 1 hour at 25°C with 4 ml of N hydrochloric acid per g
of zeolite. The resulting hydrogen Nu-10 was washed with
10 ml of distilled water per g of zeolite, dried overnight
30 at 120°C , and calcined in moist air for 6 hours at 450°C .
Its X-ray diffraction data were still substantially as
given in Table 4.

Example 3

- This Example was the same as Example 1 except that TEPA
35 was replaced by a molar equivalent of triethylene tetra-
mine (TETA). The product after 3 days at 180°C was
sodium TETA NU-10, as shown by X-ray data given in Table 5.

TABLE 4

| | | | | | | | | |
|----------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| dA | 10.9 | 9.94 | 8.76 | 6.97 | 5.373 | 4.575 | 4.353 | 4.095 |
| 100 ^I /I ₀ | 40 | 11 | 6 | 11 | 9 | 10 | 100 | 26* |
| dA | 3.663 | 3.619 | 3.466 | 2.988 | 2.818 | 2.522 | 2.493 | 2.439 |
| 100 ^I /I ₀ | 94 | 74 | 31 | 8 | 8* | 26 | 5* | 8 |
| | | | | | | | | 2.368 |
| | | | | | | | | 6 |

* due at least in part to α-cristobalite

TABLE 5

| | | | | | | | |
|----------------------------------|-------|-------|-------|-------|-------|-------|-------|
| dA | 10.9 | 6.97 | 5.373 | 4.564 | 4.353 | 4.086 | 3.678 |
| 100 ^I /I ₀ | 11 | 13 | 10 | 10 | 100 | 32* | 90 |
| dA | 3.619 | 3.480 | 2.818 | 2.522 | 2.495 | 2.436 | 2.362 |
| 100 ^I /I ₀ | 72 | 34 | 25 | 22 | 9* | 11 | 10 |

* due at least in part to α-cristobalite

Example 4

This example demonstrates that if high levels of TETA are employed then reaction times must be reduced or substantial contamination by α -cristobalite occurs. The Example was exactly as Example 3 but 94.9g of TETA were used instead of 27.2g which corresponds to an increase in the Q/SiO_2 ratio of from 0.28 to 0.94. The product after 2 days was Nu-10 with about 5% cristobalite as an impurity, but after 3 days the α -cristobalite level had increased to about 25%

Example 5

This example illustrates that zeolite Nu-10 can be prepared from mixtures containing very little free alkali e.g. $M^1OH/SiO_2 = 0.0099$. The molar composition of the mixture was:

18 TEPA, 0.48 Na_2O , Al_2O_3 , 96.3 SiO_2 , 3600 H_2O , 54 NaCl, 1.82 Na_2SO_4 .

18g TEPA were dispersed in 152g colloidal silica. Next 1.5g sodium aluminate (1.19 Na_2O , Al_2O_3 , 1.29 H_2O) dissolved in 10 g water were stirred in, followed by 24.3g sodium chloride and 1.4g concentrated sulphuric acid in 458 g water. The reaction was carried out as in Example 1, except that the reaction time was 3½ days. The product was an excellent sample of zeolite Nu-10.

Example 6

This Example illustrates that for some reaction mixture compositions with SiO_2/Al_2O_3 ratio greater than about 200, zeolite Nu-10 can be very heavily contaminated. The molar composition of the reaction mixture was:

7.36 Na_2O , 281 TETA, Al_2O_3 , 300 SiO_2 , 11293 H_2O , 166 NaCl.

The mixture was reacted at 180°C for 3 days with stirrer speed 500 rpm and the product contained about 60% α -quartz and approximately equal amounts of zeolite Nu-10, zeolite Nu-4 and α -cristobalite. The products after 1 and 2 days contained only amorphous materials.

Example 7

Sodium tetraethylene pentamine Nu-10 was prepared as follows:

Solution A

- 5 142 g SYTON X30 colloidal silica (Monsanto chemicals of molar composition $27 \text{ Na}_2\text{O} : 2400 \text{ SiO}_2 : \text{Al}_2\text{O}_3 : 19550 \text{ H}_2\text{O}$)
37.8 g Tetraethylenepentamine (TEPA) - "Technical" grade (British Drug Houses).

10 Solution B

- 1.6 g Sodium Aluminate ("Technical" grade, British Drug Houses, of molar composition $1.22 \text{ Na}_2\text{O} : \text{Al}_2\text{O}_3 : 1.02 \text{ H}_2\text{O}$)
10 g Deionised water

15 Solution C

- 22.5g Sodium chloride ("Analar" grade, British Drug Houses)
388g Deionised water

This reaction mixture had the following molar composition:

- 20 $2.14 \text{ Na}_2\text{O} : 84 \text{ SiO}_2 : \text{Al}_2\text{O}_3 : 25 \text{ TEPA} : 48 \text{ NaCl} : 3421 \text{ H}_2\text{O}$

- Solution A was introduced into a one litre 316 stainless steel autoclave, equipped with an air driven magnedrive turbine stirrer (manufactured by Autoclave Engineers).
Solution B was added with stirring at ambient temperature.
25 Solution C was then added with stirring until a homogeneous gel was produced. After sealing the autoclave, the reaction mixture was maintained under autogenous pressure with stirring (approximately 1000 rpm) at 180°C for 5 days.
At the end of this time, the reaction mixture was cooled
30 to room temperature and the product filtered and washed with deionised water (3 litres) and dried for several hours at 150°C , yield ca. 40g.

Examination of the crystals by scanning electron microscopy (SEM) showed these to be needles of uniform

width of 500 Å and lengths varying between $\frac{1}{2}$ and 1μ .

The product exhibited an X-ray powder diffraction pattern

as shown in Table 6 and the following elemental analyses :

Carbon 2.84 wt%, Hydrogen 0.67 wt%, Nitrogen 1.65 wt%,

5 Silicon 42.9 wt%, Aluminium 0.95 wt%. The product had
a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 87.

TABLE 6

X-Ray data of Sodium T.E.P.A. Nu-10 Prepared as described
in Example 7

10

| Interplanar Spacing d (Å) | Relative Intensity 100 I/I ₀ |
|--------------------------------|--|
| 10.77 | 49 |
| 8.66 | 19 |
| 6.91 | 19 |
| 5.40 | 13 |
| 4.53 | 16 |
| 4.33 | 100 |
| 4.07 | 69* |
| 3.66 | 98* |
| 3.62 | 85 |
| 3.46 | 36 |
| 2.51 | 58* |
| 2.43 | 14 |
| 2.37 | 9 |
| 1.87 | 8 |
| 1.60 | 8 |
| 1.43 | 9 |

15

20

25

30

* due at least in part to α -cristobalite

The hydrogen form of Nu-10 was prepared by calcining
10g of the above product in air at 450°C for 17 hours,
then exchanging at ambient temperature with 0.1 molar
hydrochloric acid solution (ca. 300 cm³) for several
35 hours and finally drying at 150°C for 3 hours. This

hydrogen Nu-10 had the following elemental analysis.
Carbon 0.44 wt%, Hydrogen 0.31 wt%, Nitrogen < 0.02 wt%,
Silicon 44.4 wt%, Aluminium 0.94 wt%. $\text{SiO}_2/\text{Al}_2\text{O}_3$ was 91.

Example 8

- 5 The reaction was carried out as in Example 7 with the exception that 1.6g NALFLOC sodium aluminate (of molar composition $1.23 \text{ Na}_2\text{O} : \text{Al}_2\text{O}_3 : 2.8 \text{ H}_2\text{O}$) was used at a reaction temperature of 150°C for $3\frac{1}{2}$ days. The reaction mixture had the following molar composition:

- 10 $2.24 \text{ Na}_2\text{O} : 95 \text{ SiO}_2 : \text{Al}_2\text{O}_3 : \text{T E P A} : 53 \text{ NaCl} : 3852 \text{ H}_2\text{O}$

- The product was shown by S.E.M. to be 1000 to 1500 Å diameter by 2 to 3 μ long needles and exhibited the X-ray powder diffraction of sodium T E P A Nu-10 as shown in
15 Table 7. It was calcined and exchanged as in Example 7. The respective X-ray data of the resulting sodium/hydrogen Nu-10 and the hydrogen Nu-10 are also included in Table 7.

Example 9

- The reaction was carried out as in Example 7 with the exception that the reaction was at a temperature of 150°C for 4 days. The product was shown to be 500 to 1000 Å diameter by 1 to 2 μ long needles by S.E.M. and exhibited an X-ray powder diffraction as shown in Table 8. The product was calcined and exchanged as in Example 7.

25 Example 10

The reaction was carried out as in Example 7 with the exception that the reaction was at a temperature of 120°C for 10 days. The product exhibited an X-ray powder diffraction as shown in Table 9.

30 Example 11

The reaction was carried out as in Example 7 with the exception that 18.9g of T E P A. was used at a reaction temperature of 105°C for 40 days. The product exhibited

an X-ray powder diffraction as shown in Table 10.

Example 12

The molar composition of the synthesis mixture was

2.32 Na_2O , 90.6 TETA, Al_2O_3 , 96.3 SiO_2 , 3862 H_2O

5 94.5 g TETA were dispersed in 141.5g colloidal silica, followed by a solution of 1.6g sodium aluminate in 396.5g water. The mixture was homogenised for 30 minutes. and then transferred to a 1 litre stainless steel autoclave. The reaction was carried out as in Example 1.

10 The dried product was a very pure sample of sodium TETA Nu-10 zeolite of molar composition:

1.08 Na_2O ; 2.7 TETA, Al_2O_3 , 90 SiO_2 , 12 H_2O .

15 and consisted of rod shaped crystals with dimensions 1 μm long by 0.1 μm thick.

X-ray diffraction data is given in Table 11.

A portion of this product was calcined in air at 450°C for 72 hours. The resulting sodium hydrogen Nu-10 had the X-ray data shown in Table 11.

20 The sample of sodium hydrogen Nu-10 was slurry exchanged for 1 hour at 60°C with 5 ml per g of normal hydrochloric acid. The product was filtered and washed twice with 10 ml/g of distilled water, dried at 120°C and finally calcined for 3 hours at 450°C in air. Its
25 molar composition was:

0.07 Na_2O , Al_2O_3 , 92.1 SiO_2

30 and it contained 0.9% w/w carbon and had the X-ray diffraction data shown in Table 11.

This hydrogen Nu-10 product consisted of needles 1.0-1.5 μm in length and 0.1 μm in thickness and there was very substantial twinning. The crystal type was C centred
35 orthorhombic with a probable space group CMCN and unit

TABLE 7

| Sodium TEPA Nu-10 | | Sodium Hydrogen Nu-10 | | Hydrogen Nu-10 | |
|-------------------|-------------|-----------------------|-------------|----------------|-------------|
| $d(A)$ | $100 I/I_0$ | $d(A)$ | $100 I/I_0$ | $d(A)$ | $100 I/I_0$ |
| 10.64 | 36 | 10.77 | 57 | 10.64 | 61 |
| 8.58 | 17 | 8.66 | 23 | 8.58 | 19 |
| 6.91 | 17 | 6.91 | 28 | 6.86 | 24 |
| 5.37 | 12 | 5.40 | 17 | 5.37 | 18 |
| 4.55 | 17 | 4.55 | 17 | 4.53 | 19 |
| 4.35 | 98 | 4.33 | 100 | 4.33 | 99 |
| 3.64 | 100 | 3.66 | 91 | 3.64 | 100 |
| 3.60 | 74 | 3.62 | 66 | 3.59 | 67 |
| 3.45 | 40 | 3.45 | 37 | 3.44 | 41 |
| 2.51 | 24 | 2.51 | 22 | 2.51 | 23 |
| 2.43 | 10 | 2.43 | 12 | 2.43 | 12 |
| 2.35 | 7 | 2.36 | 8 | 2.35 | 9 |
| 1.87 | 7 | 1.87 | 9 | 1.86 | 8 |
| 1.59 | 5 | - | - | - | - |

TABLE 8

X-ray data of Sodium T E P A Nu-10 Prepared
as described in Example 9

| Interplanar Spacing d (Å) | Relative Intensity 100 I/I ₀ |
|--------------------------------|--|
| 10.91 | 48 |
| 8.75 | 18 |
| 6.91 | 19 |
| 5.40 | 12 |
| 4.55 | 16 |
| 4.35 | 100 |
| 3.66 | 96 |
| 3.62 | 78 |
| 3.46 | 39 |
| 2.51 | 26 |
| 2.43 | 12 |
| 2.36 | 8 |

TABLE 10

X-Ray data of Sodium T.E.P.A. Nu-10
prepared as described in Example 11

| Interplanar Spacing d (Å) | Relative Intensity 100 I/I ₀ |
|--------------------------------|--|
| 10.77 | 48 |
| 8.66 | 17 |
| 6.91 | 18 |
| 5.37 | 12 |
| 4.55 | 15 |
| 4.35 | 96 |
| 3.66 | 100 |
| 3.62 | 77 |
| 3.46 | 40 |
| 2.51 | 24 |
| 2.44 | 12 |
| 2.36 | 8 |

TABLE 9

X-Ray data of Sodium T.E.P.A. Nu-10
prepared as described in Example 10

| Interplanar Spacing d (Å) | Relative Intensity 100 I/I ₀ |
|--------------------------------|--|
| 10.77 | 44 |
| 8.66 | 16 |
| 6.96 | 17 |
| 5.40 | 14 |
| 4.57 | 14 |
| 4.35 | 94 |
| 3.66 | 100 |
| 3.62 | 79 |
| 3.48 | 38 |
| 2.51 | 14 |
| 2.43 | 11 |
| 2.36 | 10 |

TABLE 11

X-ray data for Zeolite Nu-10 (Example 12)

| As-made Nu-10 | | Sodium Hydrogen Nu-10 | | Hydrogen Nu-10 | |
|---------------|----------------------------------|-----------------------|----------------------------------|----------------|----------------------------------|
| dA | 100 ^I /I ₀ | dA | 100 ^I /I ₀ | dA | 100 ^I /I ₀ |
| 11.19 | 51 | 10.92 | 78 | 10.98 | 66 |
| 8.93 | 6 | 8.76 | 14 | 8.76 | 11 |
| 6.970 | 16 | 6.971 | 20 | 6.971 | 18 |
| 5.471 | 9 | 5.439 | 13 | 5.422 | 12 |
| 4.611 | 12 | 4.576 | 13 | 4.588 | 12 |
| 4.418 | 97 | 4.375 | 100 | 4.375 | 100 |
| 3.708 | 100 | 3.693 | 92 | 3.693 | 90 |
| 3.655 | 75 | 3.626 | 63 | 3.626 | 65 |
| 3.500 | 38 | 3.467 | 34 | 3.467 | 30 |
| 3.370 | 10 | 3.347 | 8 | 3.339 | 6 |
| 3.320 | 8 | 3.303 | 7 | 3.303 | 5 |
| 2.536 | 20 | 2.526 | 20 | 2.529 | 22 |
| 2.449 | 11 | 2.439 | 9 | 2.439 | 9 |
| 2.380 | 7 | 2.374 | 6 | 2.371 | 7 |
| - | - | 2.067 | 5 | 2.072 | 4 |
| - | - | 2.038 | 5 | 1.907 | 3 |
| 1.884 | 6 | 1.870 | 3 | 1.874 | 7 |

TABLE 12

X-ray data of Potassium, sodium TEPA Nu-10 of Example 19

| 5 | Interplanar Spacing $d(\text{\AA})$ | Relative Intensity $100 \frac{I}{I_0}$ |
|----|--|---|
| | | |
| 10 | 10.79 | 59 |
| | 8.93 | 4 |
| | 8.68 | 9 |
| | 7.22 | 3 |
| | 6.93 | 12 |
| | 5.40 | 10 |
| 15 | 5.32 | 7 |
| | 4.543 | 7 |
| | 4.355 | 61 |
| | 3.665 | 87 |
| | 3.616 | 100 |
| | 3.467 | 45 |
| 20 | 3.342 | 8 |
| | 3.215 | 2 |
| | 2.971 | 3 |
| | 2.938 | 4 |
| | 3.898 | 4 |
| | 2.777 | 4 |
| 25 | 2.736 | 5 |
| | 2.518 | 14 |
| | 2.451 | 9 |
| | 2.435 | 12 |
| | 2.366 | 8 |
| | 2.066 | 4 |
| 30 | 2.037 | 5 |
| | 2.001 | 4 |
| | 1.900 | 5 |
| | 1.878 | 8 |
| 35 | | |

cell a = 13.853, b = 17.434, c = 5.040.

Example 13

The molar composition of the reaction mixture was

3.6 Na₂O, 42.6 TETA, Al₂O₃, 150 SiO₂, 6000 H₂O, 54 NaCl

5

The reaction was carried out as in Example 1. The product contained about 85% zeolite Nu-10 along with 15% α-cryptobalite.

Example 14

The molar composition of the reaction mixture was

10

1.21 Na₂O, 26 TETA, Al₂O₃, 96.3 SiO₂, 2014 H₂O, 54.8 NaCl

The reaction was carried out as in Example 1.

A sample withdrawn after 48 hours was substantially pure zeolite Nu-10, but the product after 72 hours at 180°C

15

was zeolite Nu-10 plus about 40% α-cristobalite

Example 15

The synthesis mixture had the following molar composition.

8.4 Na₂O, 57Q, Al₂O₃, 170 SiO₂, 8500 H₂O

20

51g of solid silica (Degussa Aerosil 200) were dispersed in a mixture of 24 g ethylene diamine and 740 g water.

Next, 1g sodium aluminate (1.22 Na₂O₂, Al₂O₃, 1.9 H₂O) and 5.3g sodium hydroxide were dissolved in 25g water. Finally, the

25

aluminate solution was stirred into the silica suspension and then reacted for 6 days at 150°C in a stirred stainless steel 1 litre autoclave. The product was Nu-10 having an SiO₂/Al₂O₃ of 165.

Example 16

This Example illustrates that symmetrically di-substituted ethylene diamines can be used in Nu-10 synthesis.

30

The synthesis mixture had the following molar composition

143 K₂O, 54Q, Al₂O₃, 170 SiO₂, 8000 H₂O

48g. Aerosil 200 were dispersed in a mixture of 29.5 g

N, N¹-diethyl ethylene diamine and 702g water. Next 0.75g

35

Kaiser S.A. alumina were dissolved in 7.5g potassium

hydroxide and 16.5g water. The aluminate solution was

stirred into the silica suspension and reacted for 41 hours at 180°C in a stirred 1 litre stainless steel autoclave. The Nu-10 product had a $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 169.

By contrast, when unsymmetrical N, N-diethyl ethylene diamine was used the reaction yielded a pure sample of zeolite Nu-4 of our copending application Number 8115407.

Example 17

This Example was exactly as Example 1 except that 20.5g ethylene diamine replaced the TEPA. The reaction was for 5 days at 150°C and the product was Nu-10.

Example 18

The synthesis mixture had the following molar composition.

1.89 Na_2O , 20.4Q, Al_2O_3 , 60.5 SiO_2 , 2563 H_2O , 32.0 NaCl , 1.69 H_2SO_4 .

First, 43g of TEPA and 141g colloidal silica were mixed. Next, 2.2g sodium aluminate (1.09 Na_2O , Al_2O_3 , 2.33 H_2O) dissolved in 10g water were stirred in, followed by 20g sodium chloride and 1.8g concentrated sulphuric acid in 380g water.

The effective OH/SiO_2 of this reaction was 0.007. The mix was reacted for 4 days at 180°C and the NU-10 product had a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 56.

Example 19

The synthesis mixture had the following composition. 1.22 Na_2O , 40.8 K_2O , 120 TEPA, Al_2O_3 , 500 SiO_2 , 25,000 H_2O . 46g Degussa Aerosil 200 were dispersed in 35g TEPA and 660g water. Next, 0.3g sodium aluminate (1.22 Na_2O , Al_2O_3 , 1.2 H_2O) and 7g potassium hydroxide were dissolved in 31g water, and then were mixed into the silica suspension. The mixture was reacted for 5 days at 180°C in a stirred stainless steel autoclave. The product was a highly crystalline potassium, sodium TEPA Nu10 having a $\text{SiO}_2/\text{Al}_2\text{O}_3 = 492$ and the X-ray data given in Table 12.

Examples 20-21

Example 20, was as Example 19 except that the potassium hydroxide was replaced by 10.7g rubidium hydroxide.

The product after 7 days at 180°C was rubidium, sodium TEPA Nu-10 of $\text{SiO}_2/\text{Al}_2\text{O}_3 = 500$.

Example 21 was as Example 19 except that the potassium hydroxide was replaced by 18.7g caesium hydroxide. The product after 5 days at 200°C was caesium, sodium Nu-10 plus about 10% each of α -cristobalite and zeolite ZSM-48.

Example 22

This Example was the same as Example 19 except that 1g of boric acid was added to the potassium hydroxide, sodium aluminate solution. The product after 8 days at 160°C was Nu-10 of $\text{SiO}_2/\text{Al}_2\text{O}_3 = 475$ and $\text{SiO}_2/\text{B}_2\text{O}_3 = 640$. About 10% α -cristobalite was present as an impurity.

Example 23

This Example was as Example 19 except that 1.5g antimonious oxide was stirred into the final reaction mixture. The product after 8 days at 160°C contained 0.3% w/w Sb_2O_3 .

Examples 24 - 25

In these Examples, other additives were mixed into Example 19 type reactions and reaction was for 8 days at 160°C. The additives were dissolved in the water prior to dispersing the solid silica.

In Example 24, the addition was 2g potassium chrome alum and the dried Nu-10 product had a $\text{SiO}_2/\text{Al}_2\text{O}_3 = 600$ and a $\text{SiO}_2/\text{Cr}_2\text{O}_3 = 1100$

In Example 25, the additive was 0.7g disodium hydrogen phosphate and the Nu-10 product had a $\text{SiO}_2/\text{Al}_2\text{O}_3 = 700$ and a $\text{SiO}_2/\text{P} = 830$.

Example 26

The synthesis mixture had the following molar composition
4.2 K_2O , 17 TEPA, 50 SiO_2 2500 H_2O .
46.2g Aerosil 200 were dispersed in a mixture of 49.4g
5 TEPA and 643g water. Next, 2.4g Kaiser S.A. alumina
(Al_2O_3 , $3H_2O$) was dissolved in a solution of 7.2g
potassium hydroxide in 24g water. The aluminate was
stirred into the silica dispersion and the mixture was
reacted for 8 days at $180^\circ C$. The product was potassium
10 Nu-10 having $SiO_2/Al_2O_3 = 47$.

Example 27

This example illustrates the use of HNu-10 as a catalyst
for toluene methylation. Zeolite HNu-10 was prepared as
described in Example 8.

15 Approximately 2g of this batch of HNu-10 was com-
pressed, crushed and sieved. 0.35 g of 250-500 μ HNu-10
catalyst particles were loaded into a microreactor in which
the zeolite was tested for toluene methylation with methanol
as methylating agent. Prior to contact with reactants,
20 the catalyst bed was flushed with nitrogen at $450^\circ C$ for
about 1 hour. A feed consisting of toluene and methanol
in a 3:1 molar ratio of the aromatic compound to the
alcohol was vaporised and passed over the catalyst at
450 $^\circ C$ at a WHSV of about 7.7. The progress of the reaction
25 is outlined by the results in Table 13.

The proportion of p-xylene in the xylenes fraction
is clearly considerably in excess of the equilibrium con-
centration of 24% and the selectivity to xylenes in the
methylated products is also high. The trimethylbenzenes:
30 produced in this test were predominantly 1,2,4-trimethyl-
benzene (~90%). This test, with a calcination of the
catalyst included, demonstrates that the catalyst can be
regenerated to give approximately the same level of
activity and selectivity in the conversion of toluene to
35 methylated products and, in particular, p-xylene.

TABLE 13

| Time on Stream hrs | Conversion of Toluene to methylated product wt % | Mol % of Methylated Product | | Wt % p-xylene in xylenes fraction |
|--------------------------|--|-----------------------------|-------------------|--------------------------------------|
| | | Xylenes | Trimethylbenzenes | |
| 1.75 | 16.1 | 91.2 | 8.8 | 63.9 |
| 13.00 | 6.5 | 94.6 | 5.4 | 62.7 |
| 25.00 | Reactant flow ceased; after N ₂ flush, the catalyst was calcined in the reactor at 530°C for 16 hours with about 60 ml m ⁻¹ flow of air. | | | |
| 1.35* | 17.2 | 90.6 | 9.4 | 64.0 |

*after recommencement of reactant mixture flow, reactor temp. 450°C

Example 28

This Example illustrates the use of HNu-10 as a catalyst for toluene methylation. Zeolite HNu-10 was prepared as described in Example 9.

5 Approximately 2g of this batch of HNu-10 was compressed, crushed and sieved. 0.37 g of 250-500 μ HNu-10 catalyst particles were loaded into a microreactor and tested in a similar fashion to that described in Example 16 except that the WHSV was about 7.4. The progress of
10 the reaction is outlined by the results in Table 14.

It is clear that the proportion of p-xylene in the xylenes fraction is considerably in excess of the equilibrium concentration of 24% and the selectivity to xylenes in the methylated products is also high. The
15 trimethylbenzenes produced in the test were predominantly 1,2,4-trimethylbenzene (\sim 90%).

The results of this test are thought to be characteristic of a relatively pure specimen of HNu-10.

Example 29

20 This Example illustrates the use of HNu-10 as a catalyst for toluene methylation. The HNu-10 used in this test was prepared using triethylenetetramine as described in Example 12.

Approximately 2g of this HNu-10 was compressed,
25 crushed and sieved. 0.34 g of 250-500 μ catalyst particles were loaded into a microreactor and heated to 450°C in a stream of nitrogen. A feedstock consisting of toluene and methanol in a 3:1 molar ratio was reacted with the catalyst in the microreactor in a similar way to
30 that described in Example 16, except that the flow rate was equivalent to a WHSV of about 9.25. The progress of this test, carried out at approximately atmospheric pressure, is outlined by the results in Table 15.

It is clear that the proportion of p-xylene in
35 the xylenes fraction is considerably in excess of the

TABLE 14

| Time on Stream hrs | Conversion of Toluene to methylated product wt % | Mol % of Methylated Product | | Wt % p-xylene in xylenes fraction |
|--------------------------|---|-----------------------------|-------------------|--------------------------------------|
| | | Xylenes | Trimethylbenzenes | |
| 3.85 | 28.2 | 87.1 | 12.9 | 59.2 |
| 4.85 | 25.1 | 88.2 | 11.8 | 62.8 |
| 5.75 | Reactant mixture flow stopped; the catalyst was purged for 16 hours with nitrogen at 450°C. | | | |
| 3.50* | 23.4 | 89.9 | 10.1 | 61.7 |

* After recommencement of reactant mixture flow to catalyst.

TABLE 15

| Time on stream hrs | Toluene Conversion wt % | Mol % methylated products | | Mol % p-xylene in xylenes fraction |
|--------------------------|----------------------------|---------------------------|-------------------|---------------------------------------|
| | | Xylenes | Trimethylbenzenes | |
| 3.3 | 19.4 | 92.0 | 8.0 | 58.9 |
| 6.1 | 16.2 | 92.1 | 7.9 | 57.6 |

equilibrium concentration of 24% and the selectivity to xylenes in the methylated products is also high.

Example 30

5 This Example is used to illustrate the effectiveness of HNu-10 as a catalyst for toluene disproportionation. The HNu-10 used in this test was that prepared in Example 8.

10 Approximately 2g of this HNu-10 was compressed, crushed and sieved. 0.38 g of 250-500 μ HNu-10 catalyst particles were loaded into a microreactor and heated to 530°C in a stream of nitrogen. The sample was maintained at this temperature in a stream of nitrogen for a further hour before toluene was passed to the catalyst. Toluene was vaporised and fed to the catalyst at a rate equivalent to a WHSV of 11.1. The progress of this test, carried out at approximately atmospheric pressure and with neat toluene feed, is outlined by the results given in Table 16.

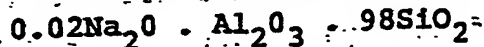
TABLE 16

| Time on stream hrs | Toluene Conversion wt % | Mol % p-xylene in Xylenes fraction |
|--------------------|-------------------------|------------------------------------|
| 1.0 | 5.4 | 31.9 |
| 3.1 | 0.7 | 51.2 |

30 It will be evident that the amount of p-xylene present in the xylenes fraction is greater than that found in an equilibrium mixture (\sim 24% p-xylene) but the catalyst shows relatively low activity for toluene disproportionation.

Example 31

A sample of sodium TEPA Nu-10 prepared as described in Example 8 was calcined at 550°C for 16 hours in air. The calcined material was then slurry-exchanged with 50 ml N/1 NH₄Cl per g of zeolite for 16 hours at 100°C. The sample was filtered, washed with distilled water and then dried at 110°C. The NH₄-NU-10 was then calcined at 550°C for 16 hours in air to produce H-Nu-10. Chemical analysis of the resulting material indicated that it had the following molar composition ignoring hydrogen:



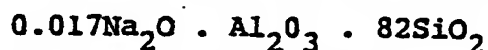
In a continuous flow reactor, about 1 g of the catalyst, particle size 710-1000 μ , was tested for methanol conversion. The catalyst was activated at 450°C under helium for 1 hour. The temperature was reduced to 400°C then methanol in helium was passed over the catalyst. The conditions and analysis of the C₁-C₄ hydrocarbons obtained can be seen in Table 17, Example 31A. After several hours, the catalyst was removed from the reactor, regenerated under air at 550°C for 16 hours then re-tested for methanol conversion. The conditions used and distribution of the C₁-C₄ hydrocarbons obtained can be seen in Table 17, Example 31B.

TABLE 17

| | Ex 31A | Ex 31B |
|---|--------|--------|
| Temp/°C | 400 | 400 |
| Conc of Methanol in Helium | 20% | 18% |
| WHSV Methanol | 1 | 1 |
| Conversion | 100% | 100% |
| Distribution % (w/w) C ₁ -C ₄ Hydrocarbons Obtained | | |
| Methane | 2.9 | 1.7 |
| Ethane | - | - |
| Ethylene | 6.9 | 7.4 |
| Propane | 6.0 | 6.4 |
| Propylene | 44.6 | 42.7 |
| Butanes | 3.0 | 3.3 |
| Butylenes | 36.7 | 38.5 |

Example 32

A sample of sodium TEPA Nu-10 prepared as described below was calcined and ion-exchanged by a procedure similar to that described in Example 1. Chemical analysis of the resulting material indicated that it had the following molar composition ignoring hydrogen:



In a continuous flow reactor, about 1 g of the catalyst, particle size 710-1000 μ , was tested for methanol conversion. The catalyst was activated at 450°C under helium for 1 hour then methanol in helium was passed over the catalyst. The reaction conditions and analysis of the C_1 - C_4 hydrocarbons obtained can be seen in Table 18, Example 32A. After examination, the catalyst was removed from the reactor, regenerated under air at 550°C for 16 hours then re-tested for methanol conversion. After activation at 450°C for 1 hour under helium, the temperature was decreased to 350°C then 55% methanol in helium was passed over the catalyst. Reaction details and analysis of the C_1 - C_4 hydrocarbons produced can be seen in Table 18, Example 32B.

TABLE 18

| | <u>Ex 32A</u> | <u>Ex 32B</u> |
|---|---------------|---------------|
| Temp/°C | 450 | 350 |
| 25 Conc of Methanol in Helium | 65% | 55% |
| WHSV Methanol | 1 | 1 |
| Conversion | 100% | >90% |
| Distribution % (w/w) C_1 - C_4 hydrocarbons obtained. | | |
| Methane | 13.4 | 9.5 |
| 30 Ethane | 1.7 | 1.4 |
| Ethylene | 11.3 | 3.5 |
| Propane | 13.0 | 20.3 |
| Propylene | 34.6 | 28.9 |
| Butanes | 1.3 | 6.1 |
| 35 Butylenes | 24.8 | 30.4 |

For the preparation of the zeolite Nu-10, the reaction mixture had the following composition :

2.3 Na₂O, 27.5 TEPA, 94SiO₂, 3800H₂O, 53 NaCl
58 g tetraethylenepentamine were dispersed in 215 g Syton X-30 of molar composition 31.65Na₂O, Al₂O₃, 2409SiO₂, 21076H₂O, followed by a solution of 2.1 g sodium aluminate (1.22 Na₂O, Al₂O₃, 1.2H₂O) in 10 g water. Finally, a solution of 34.5 g sodium chloride in 598 g water was stirred in. Stirring continued for 30 minutes to homogenize the mixture. The reaction was carried out in a 1 litre stirred stainless steel autoclave for 114 hours at 150°C. After filtration, washing and drying, the product was sodium TEPA - Nu-10 with no detectable impurities other than a slight trace of sodium chloride.

Example 33

A sample of Nu-10 prepared and activated as in Example 32 was further tested for aromatics production from methanol. A mixture of methanol in nitrogen (65% methanol) was passed over the catalyst at 450°C. The reaction conditions and hydrocarbon analysis are given in Table 19.

TABLE 19

| | |
|--------------------------------------|---|
| Temperature/°C | 450 |
| Conc of methanol % in nitrogen | 65 |
| WHSV Methanol | 1 |
| Methanol conversion % | 100 |
| The hydrocarbons produced comprised: | C ₁ -C ₅ aliphatics 92 wt % |
| | Aromatics 7 wt % |
| | Higher aliphatics traces |
| Analysis of the aromatics showed: | Benzene 1.5% |
| | Toluene 16% |
| | Ethylbenzene 3.5% |
| | Xylenes 40% |
| | C ₉ aromatics 39% |

Example 34

The reaction mixture had the following molar composition:

- 5.9 K_2O , 10 TEPA, Al_2O_3 , $30SiO_2$, 1500 H_2O
- 5 45g Aerosil 200 were dispersed in a mixture of 47.3g TEPA and 650g water. Next, 3.9g alumina were dissolved in 16.6 KOH and 27g water. The aluminate solution was stirred into the slurry and the mixture was reacted for 64 hours at $180^\circ C$. The product was potassium TEPA
- 10 Nu-10 containing traces α cristobalite and a ZSM5 type zeolite. The SiO_2/Al_2O_3 ratio of this product was 25.

CLAIMS

1. A synthetic zeolite material having a molar composition expressed by the formula:

$0.5 \text{ to } 1.5 \text{ R}_2\text{O} : \text{Y}_2\text{O}_3 : \text{at least } 20 \text{ XO}_2 : 0 \text{ to } 4000 \text{ H}_2\text{O}$
 wherein R is a monovalent cation or $1/n$ of a cation of valency n, X is silicon and/or germanium, Y is one or more of aluminium, iron, chromium, vanadium, molybdenum, arsenic, antimony, manganese, gallium or boron, and H_2O is water of hydration additional to water notionally present when R is H, and having an X-ray pattern substantially as set out in Table 1.

2. A synthetic zeolite material according to claim 1 having a molar composition expressed by the formula:

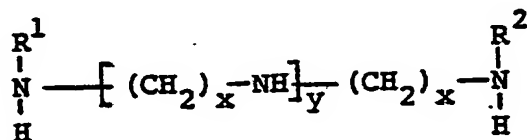
$0.5 \text{ to } 1.5 \text{ H}_2\text{O} : \text{Y}_2\text{O}_3 : \text{at least } 60 \text{ XO}_2 : 0 \text{ to } 200 \text{ H}_2\text{O}$

3. A synthetic zeolite material according to claim 1 having a molar composition expressed by the formula:

$0.5 \text{ to } 1.5 \text{ H}_2\text{O} : \text{Y}_2\text{O}_3 : 20 \text{ to } 5000 \text{ XO}_2 : 0 \text{ to } 4000 \text{ H}_2\text{O}$

4. A synthetic zeolite material according to any one of claims 1 to 3 wherein R is or includes hydrogen.

5. A method of making a synthetic zeolite material as defined in claim 1 which comprises reacting an aqueous mixture containing at least one oxide XO_2 , at least one oxide Y_2O_3 and at least one polyalkylene polyamine having the formula



wherein each of R^1 and R^2 , independently, represent hydrogen or a C_1 - C_6 alkyl group, x is an integer from 2 to 6 and y is an integer from 0 to 10, provided that when y is 0, x is from 2 to 5.

6. A method according to claim 5 wherein the aqueous mixture has the molar composition:

| | |
|---------------|------------------|
| XO_2/Y_2O_3 | 25 to 5000 |
| M^1OH/XO_2 | 10^{-8} to 1.0 |
| H_2O/XO_2 | 10 to 200 |
| Q/XO_2 | 0.05 to 4 |
| M^2Z/XO_2 | 0 to 4 |

wherein X and Y have the meanings given in claim 1, each of M^1 and M^2 , independently, is an alkali metal, ammonium or hydrogen, Q is the polyalkylene polyamine and Z is a strong acid radical.

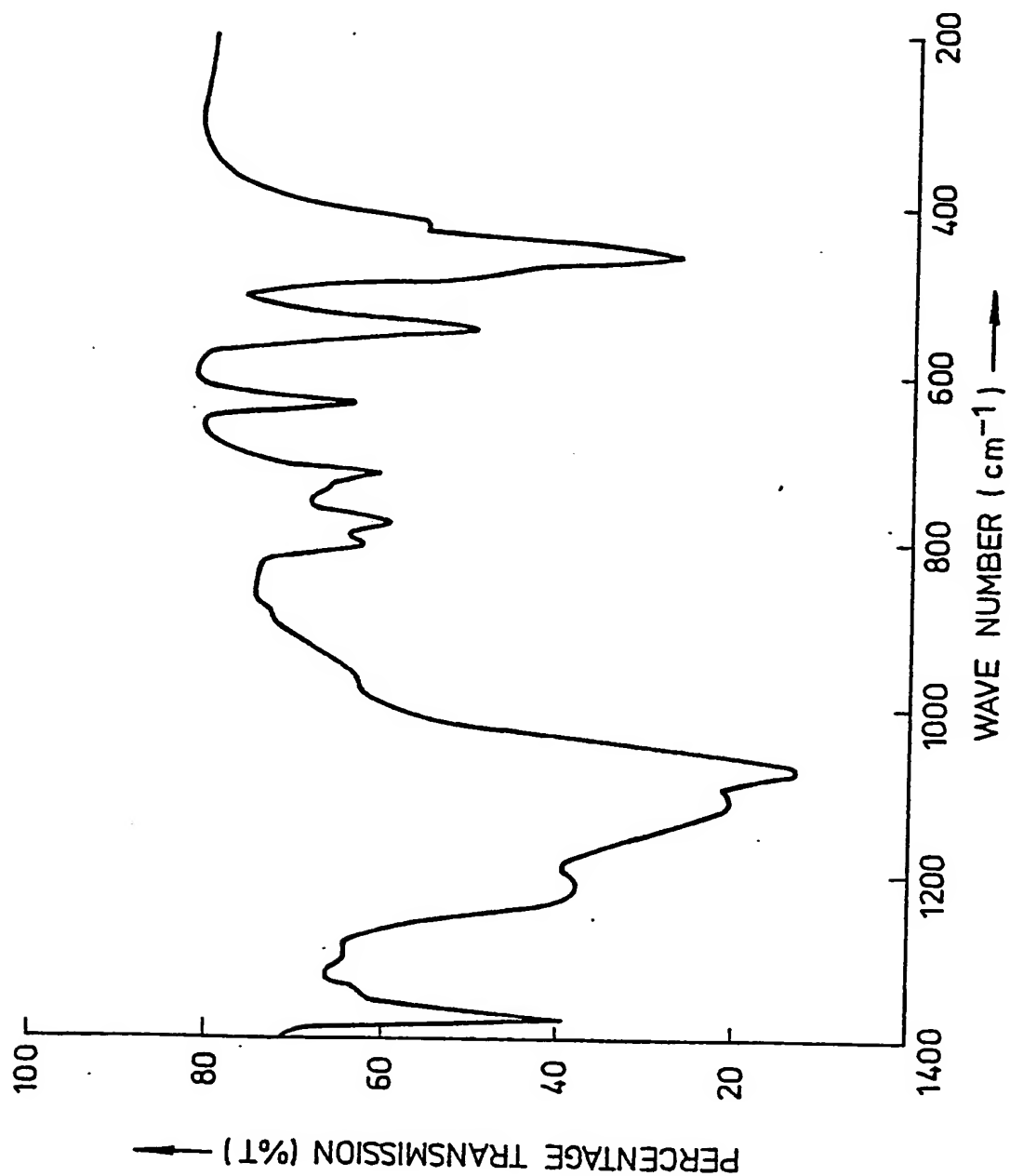
7. A method according to claim 6 wherein XO_2/Y_2O_3 is in the range 40 to 1000.
8. A method according to claim 7 wherein XO_2/Y_2O_3 is in the range 80 to 500.
9. A method according to any one of claims 5 to 8 wherein the polyalkylene polyamine is triethylene tetramine or tetraethylene pentamine.
10. A catalyst comprising a synthetic zeolite material as claimed in any one of claims 1 to 4.
11. A catalytic process employing the catalyst claimed in claim 10.
12. A process according to claim 11 wherein an alkylbenzene or a mixture of alkylbenzenes is reacted with an alkylating agent under alkylation conditions.
13. A process according to claim 12 wherein toluene is reacted with methanol to form a mixture of xylene isomers.
14. A process according to claim 11 wherein a lower monohydric alcohol or an ether derived therefrom is converted to hydrocarbons.
15. A process according to claim 14 wherein methanol or dimethyl ether is converted to lower olefins.

K STEPHENSON

AGENTS FOR THE APPLICANT

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